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New functional polymers for alternative energy applications

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New Functional Polymers for Alternative Energy Applications

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Challenges in 21st Century: Energy

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Sustainable Energy Production

- We need **clean**, **efficient**, **renewable**, **reliable** energy production technology
- Current major source of energy production: Fossil fuel
  (example: natural gas, oil)
- Fossil fuel: organic compounds composed of **C** and **H**
- Energy production from fossil fuel :
  - not clean, not renewable
  - smog, green house gas, regional instability, limited resource
- We are consuming fossil fuel about a million times more rapidly than the rate at which it was produced
- World petroleum production cannot be sustained, and will begin to decline in the future

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Major Petroleum-Consuming Nations

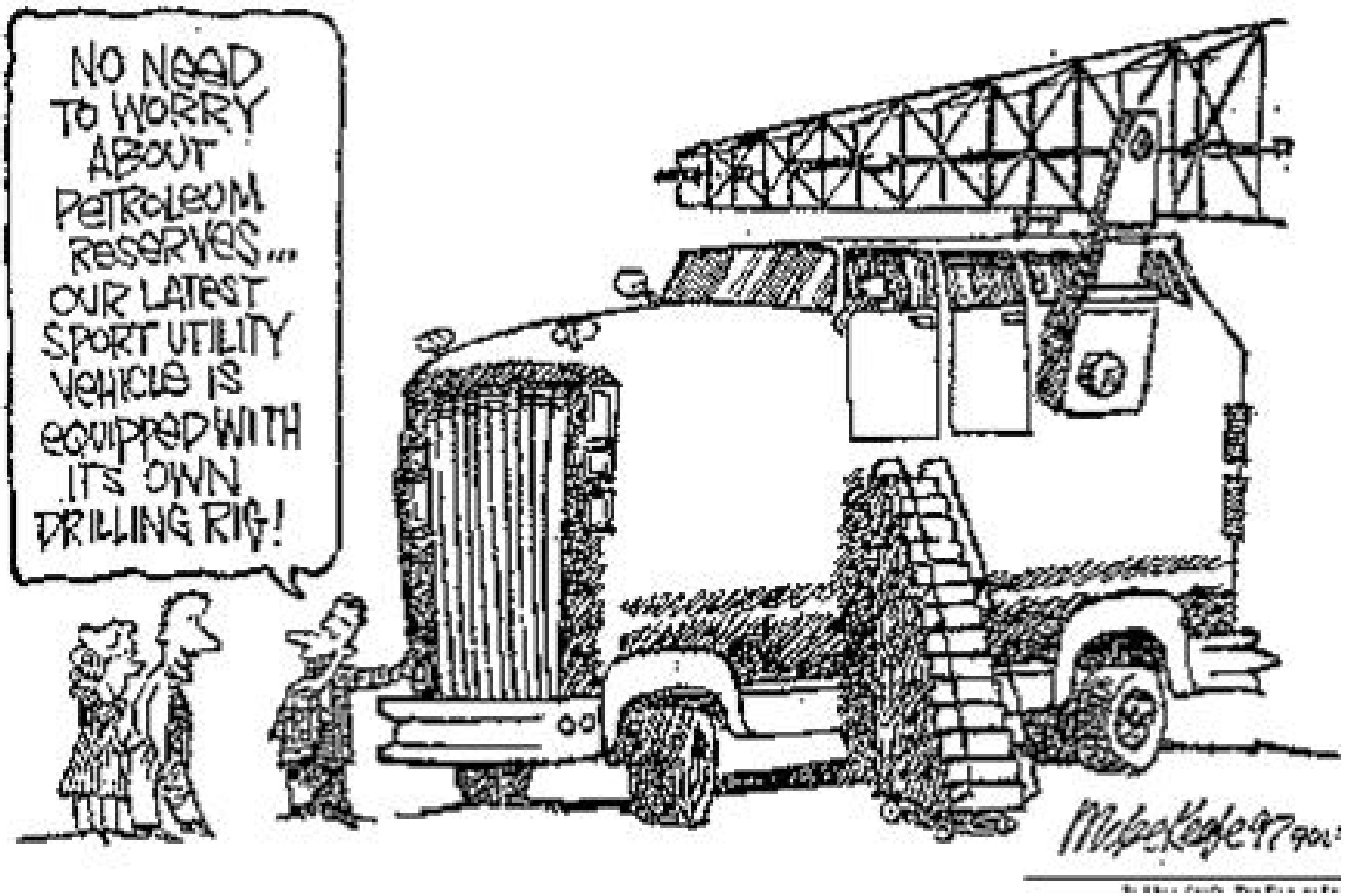
	Consumption million barrels/day	Barrels per person-day	Imports, mb/day
United States	19.7	0.0702	10.40
Japan	5.4	0.0425	5.30
China	4.9	0.0038	1.60
Germany	2.7	0.0326	2.60
UK	1.7	0.0284	–
France	1.9	0.0328	1.85
Saudi Arabia	1.36	0.0284	–

*** Energy Information Administration, DOE; www.nationmaster.com**

United States: 4% population but 25% energy consumption of the world
Among developed countries US people consumes almost two times more oil than others

Addiction to Fossil Fuels

Future Transportation Vehicle?



Alternative Energy for Our Future

Energy from non-fossil fuels

Solar energy

Wind, geothermal energy

Hydrogen fuel cells

Biomass

Interdisciplinary Research

Physics, Chemistry, Biology,

Materials Science,

Mechanical Engineering,

Electric Engineering, etc

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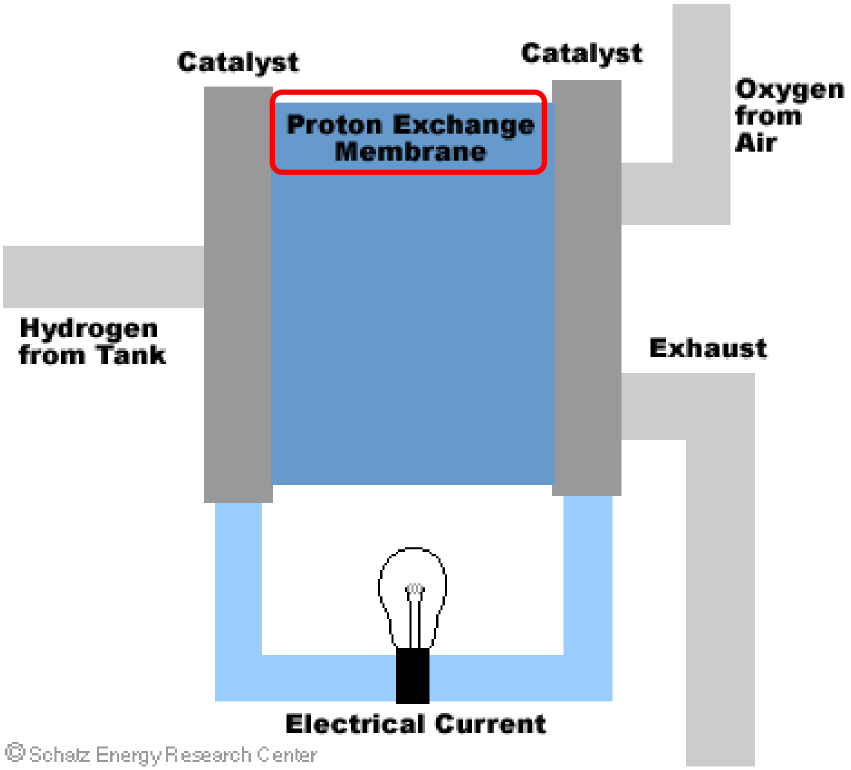
Fuel Cell, PEMFC, and PEM

- Fuel cells are **electrochemical energy conversion devices**
- Fuel cells are more energy efficient than internal combustion engine
- No need for **recharging**, operates **quickly** and **efficiently**
- **Zero emission engine** when hydrogen is used as fuel (it generates only water)



Reaction at Anode: $2\ H_2 \rightarrow 4\ H^+ + 4\ e^-$

Reaction at Cathode: $O_2 + 4\ H^+ + 4\ e^- \rightarrow 2\ H_2O$

Overall Cell Reaction: $2\ H_2 + O_2 \rightarrow 2\ H_2O$ + electricity

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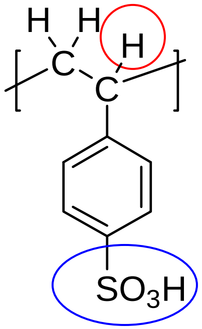
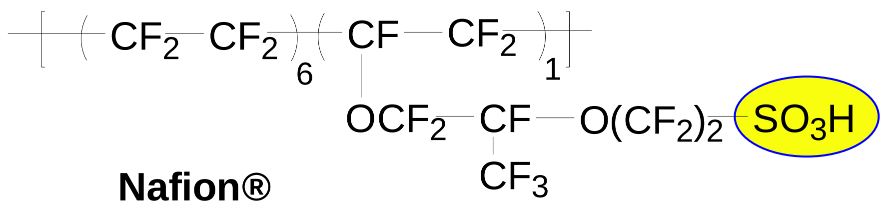
Why Need New Proton Exchange Membrane?



Cross-linked Sulfonated Polystyrene
General Electric, early 1960s
Gemini Space program, 500 h



DuPont, 1970s

Nafion®

Perfluorosulfonated tetrafluoroethylene copolymer

Good

Exceptional chemical stability (>5000 h)
High H^+ conductivity at low temperature (~100 mS/cm)

Drawbacks

Low H^+ conductivity at high temperature (>100 ^oC)
Poor mechanical stability at high temperature (>100 ^oC)
High cost
High CH_3OH permeability in DMFC

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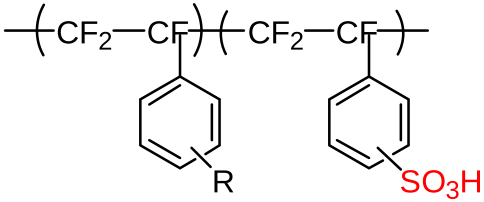
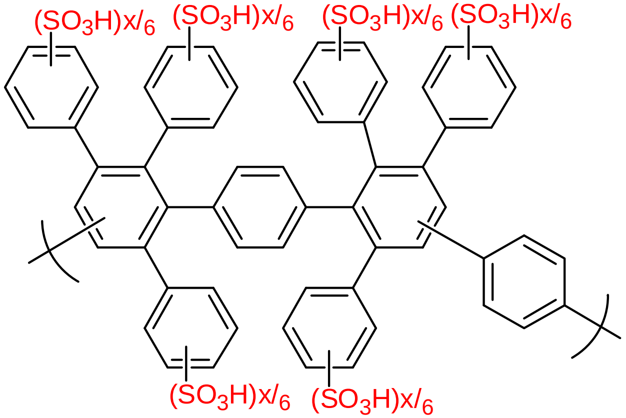
Current New Hydrocarbon-based PEMs



where R = alkyls, halogens, alkoxy, $CF=CF_2$, CN, NO_2, OH

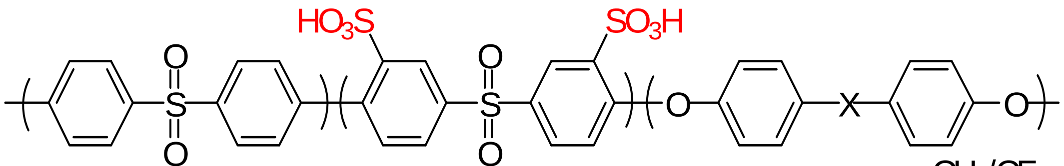
BAM3G

Ballard Advanced Materials, 1995



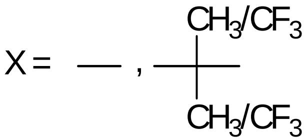
sulfonated poly(phenylene)

Sandia & Los Alamos National Labs, 2005



sulfonated poly(arylene ether sulfone)

Virginia Tech, 2001



Rigid aromatic main-chain polymer: maintain good physical properties

Attachment of SO_3H groups in aromatic rings: proton conductive moiety

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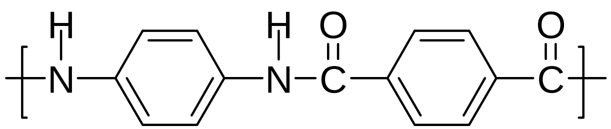
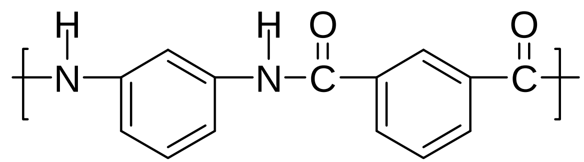
Motivation for New PEM

Aromatic polyamides



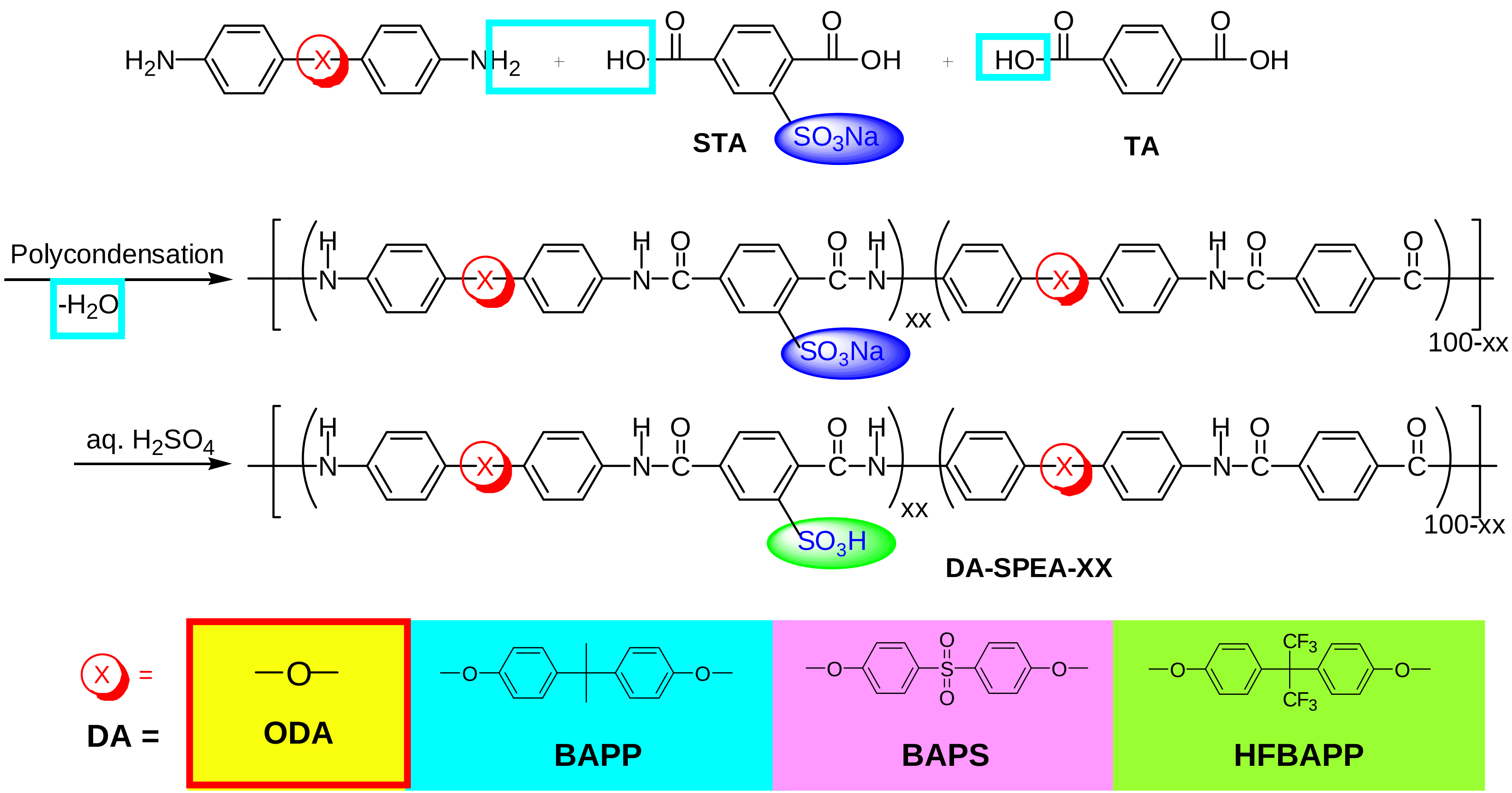
Kevlar



Nomex

- Heat-resistant and strong synthetic fibers
- Used in aerospace and military applications
- High thermal, chemical stability and good physical properties
- Thermal decomposition occurs at around 400 ^{o}C
- Lack of synthetic method for sulfonated polyamides that can be used as fuel cell membrane

Synthesis of Sulfonated Polyamides



Membrane Properties of Sulfonated Polyamides

Table 1. Intrinsic viscosity, IEC, and water uptake of sulfonated polyamides

Polymer[a]	Intrinsic Viscosity (dL/g)	IEC (mequiv/g)		Water Uptake
		Calculated	Experimental	wt%
ODA-SPEA-40	2.08	1.05	1.10	17%
ODA-SPEA-50	1.86	1.33	1.34	23%
ODA-SPEA-60	2.17	1.56	1.58	24%
ODA-SPEA-70	2.78	1.83	1.80	33%
BAPP-SPEA-70	1.86	1.06	1.17	17%
BAPS-SPEA-70	1.76	1.11	1.13	10%
HFBAPP-SPEA-70	1.40	0.94	0.99	13%

[a] Number indicates the degree of sulfonation

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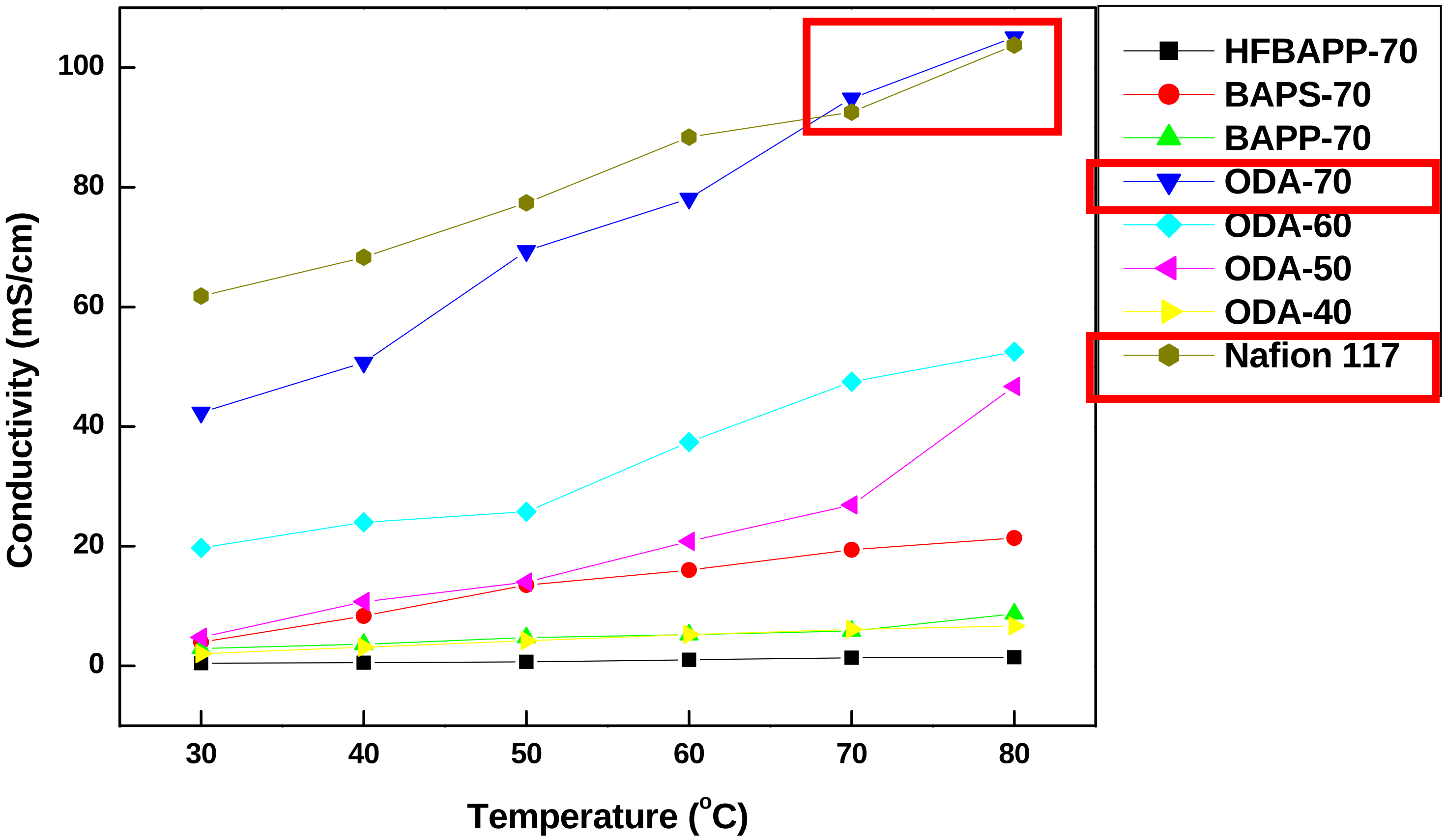
Proton Conductivities of Sulfonated Polyamides



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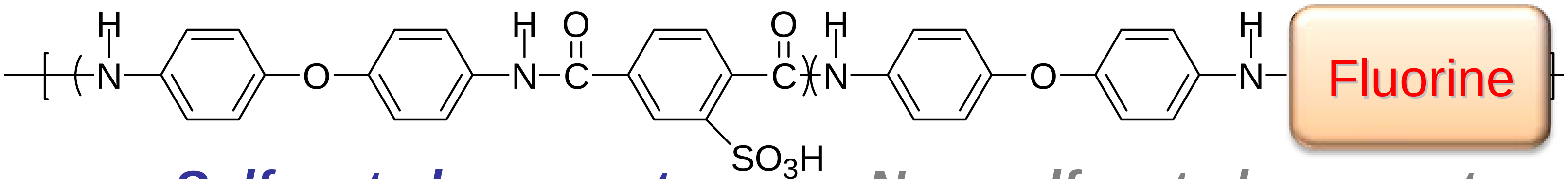
Improvement of Water Stability with Fluorine



Sulfonated segment

Non-sulfonated segment

Proton conductivity
Increase water uptake

Physical properties
Mechanical stabilities
Control water uptake

- ODA-SPEA-70 showed a comparable proton conductivity of Nafion 117 over 70 ^{o}C

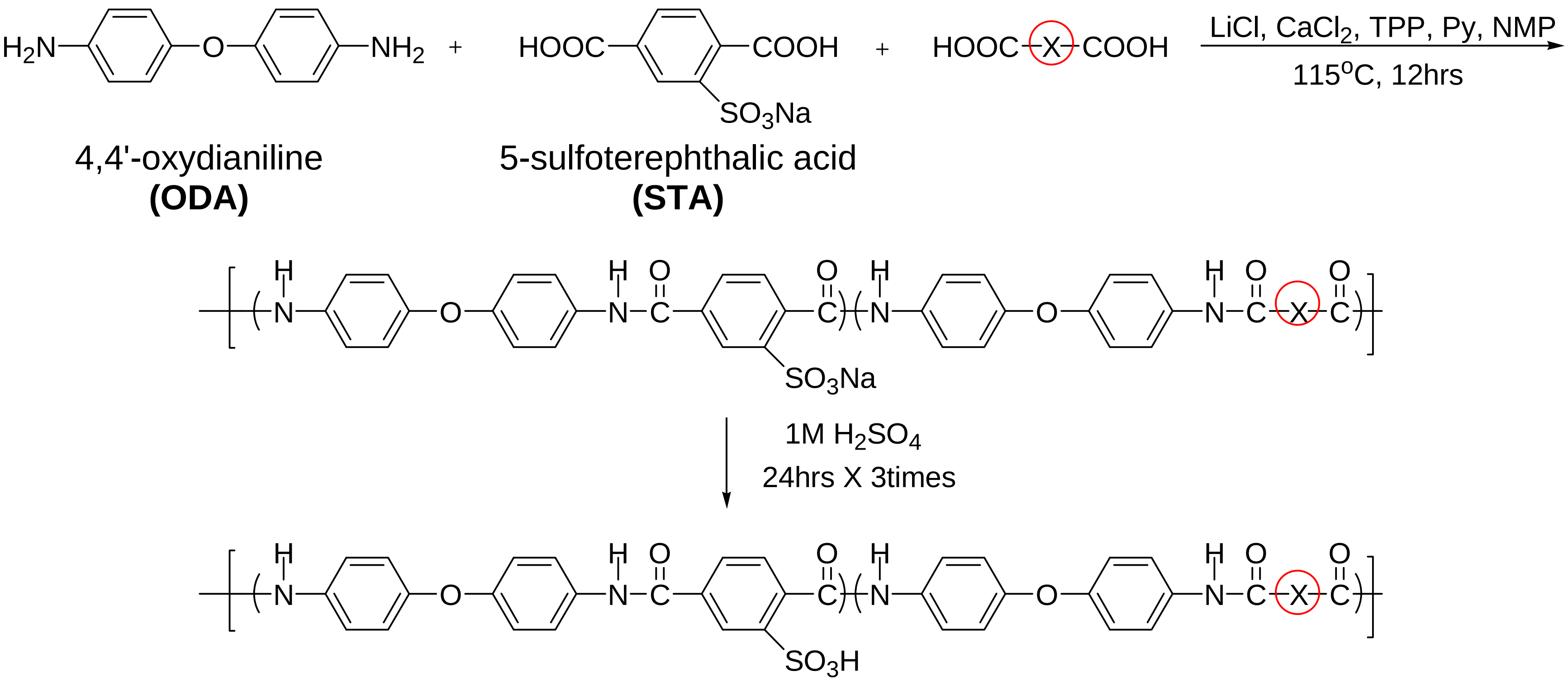
- ODA-SPEA-70 had acceptable water uptake (~30 %)

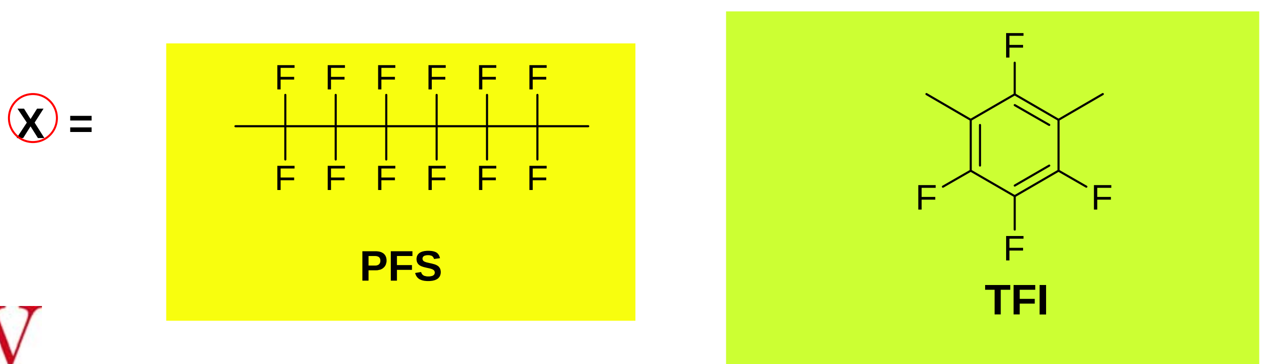
- Unfortunately, ODA-SPEA with higher degree of sulfonation (>70 %) was not stable in water

❖ Advantage of Fluorine groups

- **Reduce water uptake**
- **Improve stability in water**

Synthesis of Sulfonated Fluoropolyamides





Membrane Properties of Fluorinated Polymers

Table 2. Intrinsic viscosity, IEC, and WU of sulfonated fluoropolyamides

Polymer	Intrinsic Viscosity (dL/g)[a]	IEC (mequiv/g)		Water Uptake
		Exp	Calcd[b]	
ODA-PFS-80	1.24	1.74	1.72	8 %
ODA-PFS-90	1.50	1.99	2.00	31 %
ODA-TFI-70	1.45	1.61	1.65	20%
ODA-TFI-80	1.37	1.81	1.87	39%
ODA-TFI-90	1.35	2.05	2.09	41 %
ODA-SPEA-70	2.78	1.80	1.83	33 %
Nafion 117		0.9		~ 20 %[c]

[a] Measured in DMAc with NaI at 30 ^{o}C
[b] Calculated by feed ratio of monomers
[a] McGrath et al. *Chem. Rev.* **2004** ,104, 4587

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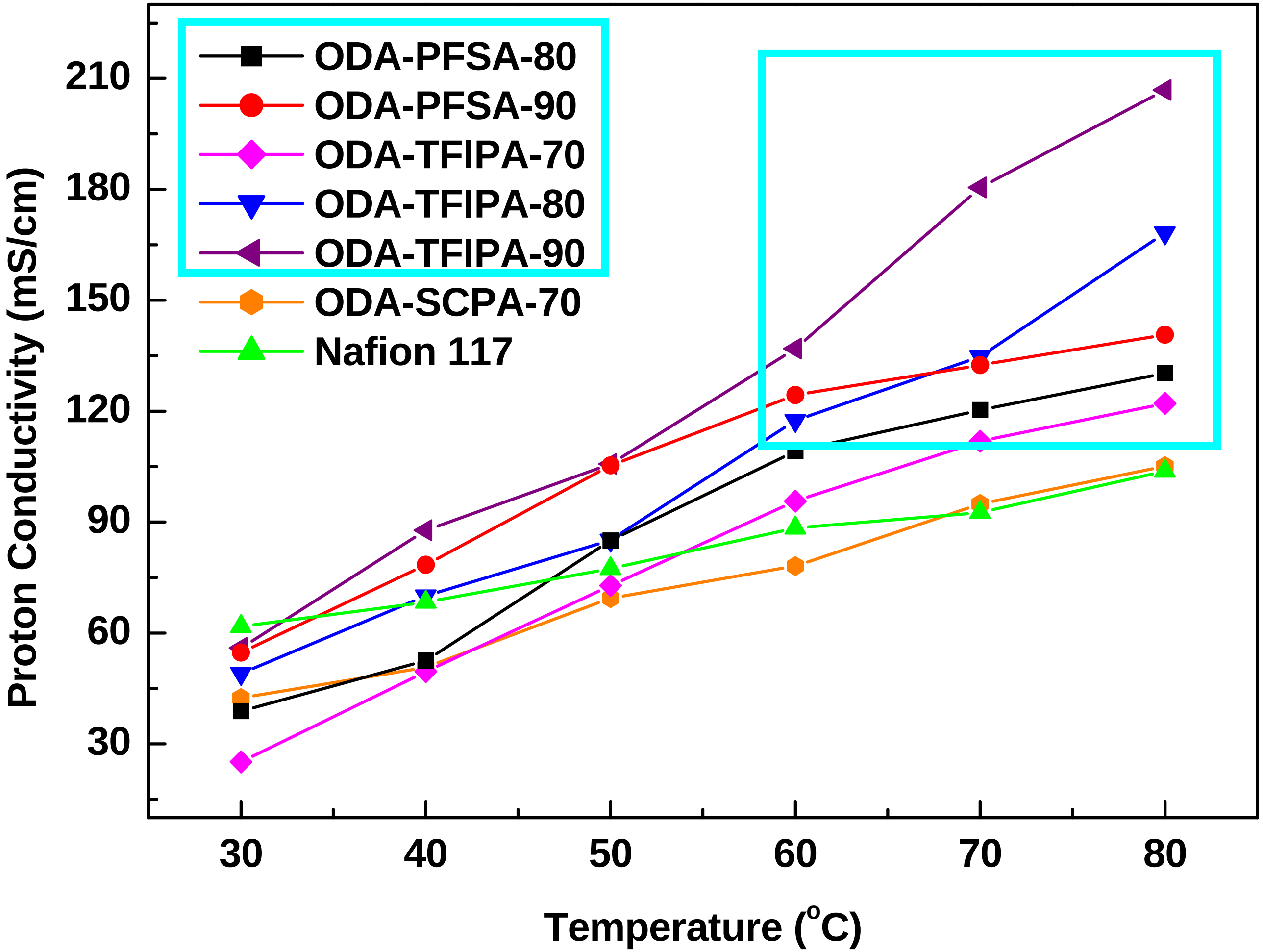
Conductivities of Sulfonated Fluoropolyamides



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Summary

- A series of high-molecular-weight sulfonated polyamides was synthesized via polycondensation

- Sulfonated polyamides showed relatively low water uptake (less than 30%) compared to other hydrocarbon-based PEMs

- ODA-SPEA-70 showed proton conductivity comparable to Nafion at 70-80 ^{o}C

- The sulfonated fluoropolyamides displayed higher proton conductivity than Nafion 117 above 60 ^{o}C

Acknowledgment

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- **Collaborations**
  - UTC Power (H_2 Fuel Cell Membrane)
  - Ceramatek Inc. (Na^+ transporting membrane for biofuel production)
- **Students and Postdocs**

  Graduate students: Jihoon Shin, Se Hye Kim, Tae Soo Jo, Lacie Brownell

  Postdocs: Dr. Ying Chang, Dr. Amit Tewari,

  Undergraduates: Coreen Ozawa, Bryce Eager, Adi Avi-Izak, Nathan Ringer
- **Instruments**

  Prof. David Hatchett and Prof. James Selsser (UNLV)

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